The Transient Oxidation Stages of Metals

Judith C. Yang, University of Pittsburgh, DMR Award#9902863

GOAL:

• Bridge the gap between surface science and corrosion.

• Understanding oxidation at the nanoscale.

EXPERIMENT:

• In situ ultra high vacuum transmission electron microscopy to visualize the initial stages of copper oxidation in real time under well-controlled conditions.

IMPACT

» environmental stability at the nanoscale, which is critical for nanodevices.

» processing of nanoscale oxides, such as in semiconductor devices, magnetic materials, and superconducting material.

» fuel cells, catalysis, corrosion.

» New paradigm for metal oxidation based on "heteroepitaxy" (thin film growth), where surfaces play the key role.

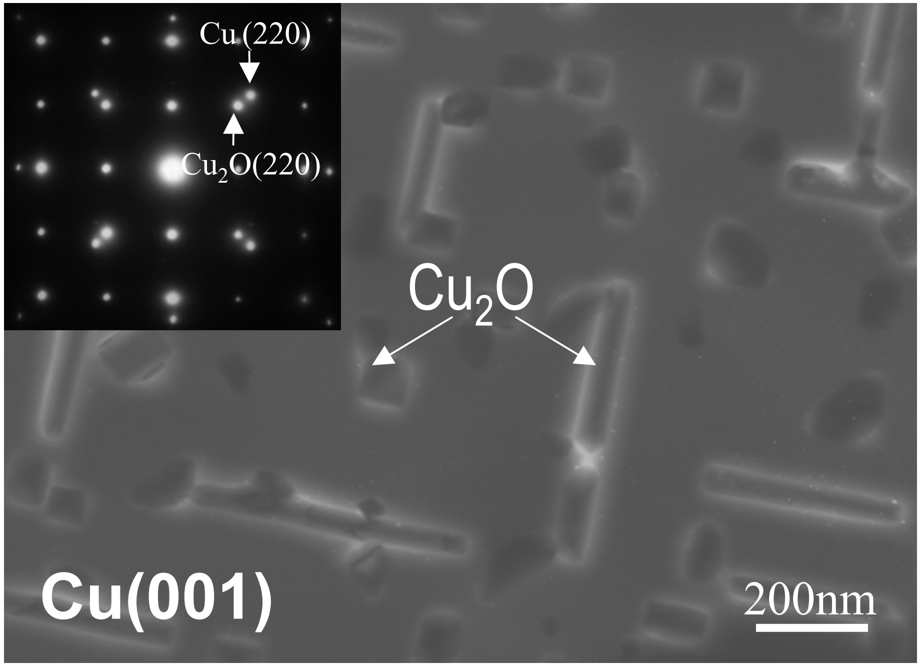

Figure: TEM image of Cu_2O formed during in situ oxidation of Cu at various temperatures.

As an example of nanoprocessing, oxide "dots" and "nanorods" can be created at selective oxidation conditions.

Surface science studies focus on the first few monolayers, whereas bulk oxidation focus on the growth of the thermodynamically stable oxide (on the order of a few microns). The goal of this program is to bridge this gap, e.g. the nucleation and initial growth of the oxide, by *in situ* UHV-TEM. Classic corrosion theory is based on thermogravimetric analysis (TGA), which measures the weight change and does not provide structural information. Hence, classic theories of oxidation (such as the Cabrera Mott theory of metal passivation) assume a uniform growing film. My goal is to provide the structural information and test classic theories. However, we find that the concepts of "heteroepitaxy" describe surprisingly well the initial stages of copper oxidation, where surface diffusion of oxygen is the key mechanism.

The *in situ* UHV-TEM is a uniquely modified TEM (at the Materials Research Lab, at the University of Illinois at Urbana-Champaign). The capabilities include: 10^{-9} torr base pressure, leak valve to introduce gases (up to 10^{-4} torr with electron gun on, 1 atm with electron gun off). Temperature range from room temperature to 1000°C, because of the modified sample holder.

The graduate student has spent 1 year at MRL-UIUC for experiments, and examined Cu(100), (110) and (111) oxidation in depth, and preliminary experiments on other metals, such as Ag, Al and Fe. He has found unique oxide structures, such as nanorods and layered terraces, depending on the oxidation conditions. (only the nanorods are shown in the figure).

The nanorod formation (T=600°C, P=8×10^{-4} torr O_2) on Cu(100) fits well with the elastic strain model proposed by Tersof and Tromp, who originated this theory to explain the shape transition in Ge on Si heteroepitaxy.

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Brief Summary of Outreach

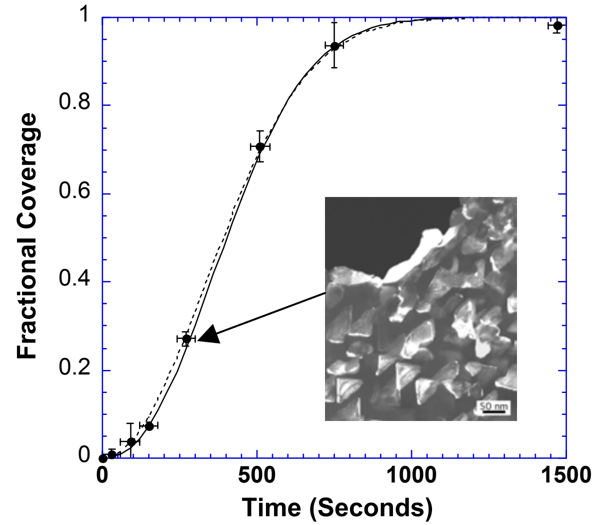
Training

1 graduate student (Guangwen Zhou),
1/3 post-doc, (Mridula Bharadwaj)

3 undergraduates
- **2 as summer projects**
- **1 as senior thesis project.**

Co-organizer of symposium on the fundamentals of oxidation and corrosion (Materials Research Society, Spring 2001).

Undergraduate Research Experience:
Computational modeling of Copper oxidation.



Publication:
Judith Yang, Dan Evan, Lori Tropia, Applied Physics Letters, accepted.

Award:
2nd place to Lori Tropia at AMS Undergraduate Poster Competition. (Pittsburgh, March, 2000)

Graduate Student, Guangwen Zhou, spent over 1 year at the Materials Research Laboratory for his training and experiments.

A post-doc, Mridula Dixit Bharadwaj (woman), modeled the water vapor effect on the surprising reduction of Cu_2O by water vapor.

The undergraduate research project (Lori Tropia and Dan Evan) was to computationally model the nucleation to coalescence behavior of the Cu oxidation at 350°C and 0.1 torr of oxygen gas. A slight modification of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory, for nucleation to coalescence, using a surface diffusion model for nucleation and growth fit surprisingly well with the experimental data (figure). The potential impact is a new theory of passivation of metals where surface diffusion is the primary mechanism. This undergraduate research experience resulted in a journal publication and a poster prize.